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(54) **Stabilized monomer compositions.**

(57) A process for stabilizing an ethylenically unsaturated monomer or oligomer from premature polymerization is disclosed whereby a stabilizing amount of an amine, preferably a substituted hindered amine, in combination with phenothiazine or other related heterocyclic moiety is added to said polymerizable monomer or oligomer. The ethylenically unsaturated monomer or oligomer encompass vinyl monomers or oligomers bearing at least one polymerizable moiety. The combination of substituted hindered amine plus phenothiazine inhibits premature polymerization in the liquid and/or vapor phase.

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The instant invention pertains to stabilized monomer compositions, in particular to compositions containing ethylenically unsaturated monomers, stabilized against premature polymerization.

The ethylenically unsaturated compounds which can be polymerized by free radical initiation are commonly called monomers. They constitute a major class of industrial chemicals. Because of the presence of the polymerizable double bond, the widespread sources of initiating radicals from peroxides, light and/or thermal generation, such monomers are prone to undesirable and premature polymerization at various stages during their manufacture, purification, storage, shipping, blending and use. Protection of such monomers from such premature polymerization is needed up to the point where polymerization is actually desired. If premature polymerization does occur, the monomer may suffer contamination by polymer, troublesome increase in viscosity, gelation and/or loss of reactivity. Fouling of distillation equipment including heat exchanger surfaces, storage vessels, transfer lines, pumps, shipping containers and application equipment can occur with ensuing costs of cleaning, downtime, loss of material and unnecessary labor costs. A particularly difficult situation is the preparation of polyol acrylates from polyols and acrylic acid since prolonged heating periods are required to complete the esterification. Premature polymerization can also constitute a safety hazard since uncontrolled exothermic polymerization can cause ruptured vessels, atmospheric contamination, and in extreme cases, explosions and fires. Deterioration of monomers in shipping and storage may also make necessary the use of costly refrigerated shipping and storage facilities.

A further problem is that of undesired polymerization of adventitious monomers, that is, radically-polymerizable unsaturated monomers which occur in commercial products such as hydrocarbon fuels and refinery streams. In these cases, polymerization accompanied by the incorporation of oxygen moieties leads to gum and sludge deposits which can foul carburetors, engines, fuel tanks or fuel lines. In refineries, the adventitious monomers in hydrocarbon streams such as cracking products can foul pipelines, valves, pumps, heat exchangers, stills and storage vessels.

Another problem in regard to undesired polymerization of free radical polymerizable monomers is the case of polymerizations which are intentional, but which must be prevented from going too far. For example, the quality of poly(vinyl chloride) suspension polymer and of synthetic rubber made from olefins and dienes is superior (i.e. better molecular weight distribution, stability, and processing properties) if the polymerization is stopped short of complete consumption of the monomers. It is also desirable to have available in a plant conducting vinyl polymerization reactions some rapid and efficient means for stopping a runaway polymerization if other means such as cooling should fail.

It is known that the addition of certain compounds to monomers can retard or even prevent their undesired polymerization, and that when polymerization of the monomer is desired, the inhibitor can be removed or overridden by a deliberately-added polymerization initiator. Various aromatic compounds have been used as such inhibitors in the prior art. Typical ones are hydroquinone, monomethyl ether of hydroquinone (MEHQ), tert-butylphenols, phenothiazine, phenylenediamines and benzoquinones. These are usually used at a level of 50 to 1000 ppm. These inhibitors are not totally effective, and even with such inhibitors present, it is often advisable to store such inhibited monomers in a cool place and for limited periods of time. Moreover, these aromatic inhibitors are a cause of serious discoloration problems in the monomers and in polymers deliberately prepared from such monomers. Typically these aromatic inhibitors produce quinoidal chromophoric groups with very high visible light absorbance. The use of stable nitroxyl radicals as inhibitors also leads to discoloration since such compounds are themselves highly colored, usually bright red.

In order to overcome these color problems, a diligent search was made to find alternative inhibitors which are both effective and not discoloring. This search led to the N,N-dialkylhydroxylamines and the N,N-diaralkylhydroxylamines. Some typical references are cited infra.

US-A-3,222,334 and US-A-3,878,181 disclose the use of N,N-dialkylhydroxylamines such as N,N-diethylhydroxylamine as short-stopping agents for emulsion polymerizations of butadiene/styrene rubber and chloroprene.

US-A-3,148,225 and US-A-3,697,470 disclose the use of N,N-dialkylhydroxylamines such as N,N-diethylhydroxylamine and N-alkyl-N-arylhydroxylamine such as N-ethyl-N-phenylhydroxylamine respectively as short-stopping agents and popcorn polymer inhibitors in processes for preparing synthetic rubber. The popcorn polymer formation is a serious problem encountered in recovering of monomers from such synthetic rubber operations.

US-A-4,782,105 teaches the use of long chain N,N-dialkylhydroxylamines as stabilizers to prevent the premature gelation of unsaturated elastomer compositions such as styrene/butadiene copolymers or polybutadiene.

US-A-3,408,422 describes the use of N,N-dialkylhydroxylamines such as N,N-diethylhydroxylamine and N,N-diaralkylhydroxylamines such as N,N-dibenzylhydroxylamine as stabilizers for preventing the premature gelation of unsaturated polyesters.

US-A-4,798,889 teaches the use of N,N-dialkylhydroxylamines such as N,N-diethylhydroxylamine or N,N-dibenzylhydroxylamine as stabilizers to reduce the thermal polymerization of organosiloxanes substituted by ethylenically unsaturated moieties.

US-A-4,409,408 and US-A-4,434,307 disclose the use of N,N-dibenzylhydroxylamine in combination with an alkylated diphenol (catechol or hydroquinone) as inhibitors to prevent the polymerization of styrene.

The use of stable nitroxyl radicals including those derived from hindered amine moieties has also been disclosed. Typical references are cited below.

SU-A-1,139,722 describes the inhibition of styrene and comonomers such as butadiene using 1-oxyl derivatives of hindered amine compounds such as N,N'-bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)adipamide. The elimination of popcorn polymer and of the clogging of equipment is touted as the result of using such 1-oxyl compounds.

JP-A-60-36501 describes the use of hindered amines and their 1-oxyl and 1-alkyl derivatives as vinyl polymerization inhibitors to improve storage stability of monomers such as acrylate and methacrylate esters.

EP-A-178,168 and GB-A-1,127,127 describe the use of 1-oxyl substituted hindered amine compounds as stabilizers for inhibiting the polymerization of α,β -ethylenically unsaturated monocarboxylic acids, such as acrylic acid, during its recovery by distillation.

US-A-4,670,131 teaches the use of 1-oxyl substituted hindered amine compounds as stabilizers for preventing the fouling of equipment for processing organic feed streams containing olefins by inhibiting the polymerization of said olefins.

In a theoretical study of the inhibiting effects of selected hindered amine compounds, Y. Miura et al., Makromol. Chem. 160, 243 (1972) disclose that 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one is highly effective in retarding the onset of the polymerization of styrene and methyl methacrylate. By contrast, the corresponding 1-benzyloxy-2,2,6,6-tetramethylpiperidin-4-one is stated to have no effect in delaying the polymerization of styrene and no retarding effect on said polymerization once begun.

US-A-4,668,721 and US-A-4,691,015 disclose the use of 1-hydroxy substituted hindered amine compounds as stabilizers for polyolefin compositions in combination with one or more other stabilizers such as phenolic antioxidants, ultraviolet light absorbers and the like.

EP-A-334,500 (Derwent 89-279844/39) describes polymerization inhibition compositions comprising (a) a phenothiazine and (b) a substituted phenylenediamine for inhibiting the polymerization of styrene.

None of these references describes or suggests that a substituted hindered amine plus phenothiazine or other related heterocyclic moiety is or could possibly be such effective inhibitors to prevent the premature polymerization of monomers in either the liquid or vapor phase.

It is the broad object of the invention to provide monomer compositions inhibited against undesired and premature polymerization by means of small, but effective amounts of selected additives which do not impart undesired color to the monomer compositions.

It is a further object of the invention to provide inhibited monomer compositions which have substantially improved stability relative to compositions inhibited by methods known in the prior art.

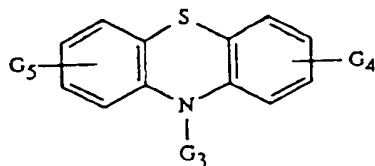
It is a further object of the invention to provide a means for short-stopping or retarding polymerization of monomers once polymerization is started.

It is a further object of the invention to provide effective inhibitors for monomers known to be difficult to inhibit such as acrylic acid.

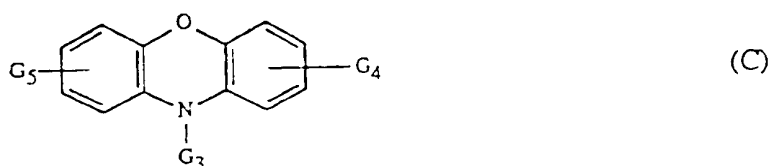
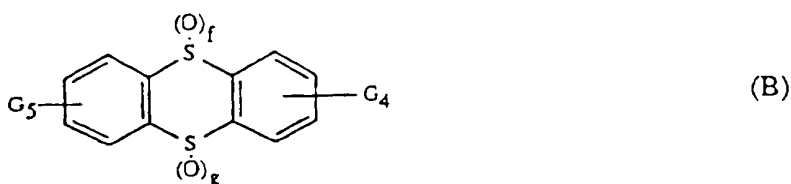
It is still a further object of the invention to provide highly effective combinations of inhibitors for said monomers.

The invention pertains to a monomer composition, stabilized against premature polymerization, which comprises

- (a) an ethylenically unsaturated monomer or mixture of monomers, polymerizable by free radical initiation, and
- (b) an effective amount, sufficient to inhibit the premature polymerization of component (a), which is a combination of
 - (i) a heterocyclic compound selected from any of formulas A to C



(A)

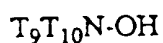
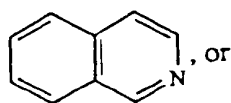
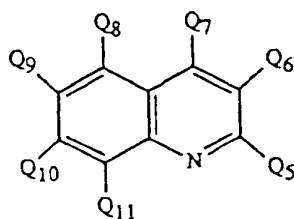
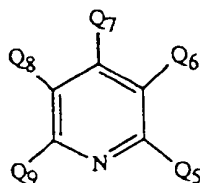
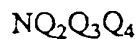


where

G₃ is hydrogen, alkyl of 1 to 4 carbon atoms or alkenyl of 3 to 4 carbon atoms, preferably hydrogen, allyl or 1-propenyl, most preferably hydrogen,

G₄ and G₅ are independently hydrogen or alkyl of 1 to 8 carbon atoms, preferably hydrogen, and f and g are independently 0, 1 or 2, and

(ii) a primary, secondary or tertiary amine, or hydroxylamine, or mixture thereof, of the formula



wherein

Q₂, Q₃ and Q₄ are independently hydrogen, alkyl of 1 to 18 carbon atoms, said alkyl substituted by hydroxy, alkenyl of 3 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by alkyl of 1 to 12 carbon atoms or by phenyl,

55 with the proviso that all of Q₂, Q₃ and Q₄ are not hydrogen, cycloalkyl, phenylalkyl or aryl at the same time; or Q₃ and Q₄ together are straight or branched alkylene of 4 to 8 carbon atoms, 3-oxapentamethylene, 3-thiapentamethylene, 3-iminopentamethylene or 3-methyliminopentamethylene, and Q₂ is hydrogen or alkyl of 1 to 8 carbon atoms;

Q_5 , Q_6 , Q_7 , Q_8 , Q_9 , Q_{10} and Q_{11} are independently hydrogen, methyl or ethyl, preferably hydrogen or methyl, most preferably hydrogen; or

T_9 is hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms or phenylalkyl of 7 to 15 carbon atoms, and

5 T_{10} is alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms or phenylalkyl of 7 to 15 carbon atoms.

The weight ratio of component (i):component (ii) is preferably from 1: 10 to 1000: 1, more preferably 1:1 to 10:1, where the total concentration is in the range of preferably 50-10,000 ppm, more preferably 200-600 ppm, based on the monomer being stabilized.

10 Preferably, component (i) is a compound of the formula (A) and, more preferably, component (i) is phenothiazine.

Component (ii) is preferably a hydroxylamine. Particularly preferred are N,N-diethylhydroxylamine or N,N-di-tert-butylhydroxylamine.

The hydroxylamine derivative may generally be prepared by oxidizing a hindered amine with a peroxy compound such as hydrogen peroxide followed by reduction of the oxyl intermediate formed to the desired hydroxylamine derivative. Such a process is taught in US-A-4,665,185.

15 The monomers of component (a) of this invention are any having at least one carbon-carbon double bond capable of undergoing free radical induced polymerization. Such monomers are well known in commerce and comprise a wide variety of structural types. Typical examples of such monomers are the olefinic hydrocarbons such as styrene, α -methylstyrene and divinylbenzene; dienes such as butadiene and isoprene; halogenated
20 monomers such as vinyl chloride, chloroprene, vinylidene chloride, vinylidene fluoride and vinyl fluoride; unsaturated acids such as acrylic acid, methacrylic acid and crotonic acid; unsaturated esters such as vinyl acetate, alkyl acrylates and alkyl methacrylates such as methyl methacrylate, ethyl acrylate, methyl acrylate, 2-hydroxyethyl acrylate and methacrylate, ethylene bismethacrylate, trimethylolpropane triacrylate, acrylated epoxy resin and polyethylene glycol diacrylate; unsaturated amides such as acrylamide, N,N-dimethylacrylamide, methylene-bisacrylamide and N-vinylpyrrolidone; unsaturated nitrile monomers such as acrylonitrile;
25 and unsaturated ethers such as methyl vinyl ether, and miscellaneous monomers such as the vinyl pyridines, diethyl vinylphosphonate and sodium styrenesulfonate.

The instant invention also pertains to the use of mixtures of said monomers and to the use of resins such as acrylate-terminated polyurethanes and unsaturated polyesters. The common feature making all of these
30 materials relevant to the present invention is the presence of a polymerizable double bond.

Also in the category of monomers are unsaturated oils such as drying oils like linseed oil, where polymerization also incorporates oxygen. There are also adventitious monomers formed in refining processes, for example polymerizable olefinic unsaturation in gasoline, jet fuel, solvents, crude oil and cracked hydrocarbon streams. The common feature of all of these substances is encompassed in the broad term "monomers" and
35 all are contemplated to be within the scope of instant component (a). Polymerization of such materials is often accompanied by autooxidation.

The acrylates, particularly acrylic acid itself, are unusually difficult to inhibit because of their inherent high polymerizability. The instant compounds are shown to be particularly effective in inhibiting acrylic acid from premature polymerization.

40 Preferably component (a) is a monomer selected from the group consisting of the olefinic hydrocarbons, dienes, halogenated monomers, unsaturated acids, unsaturated esters, unsaturated amides, unsaturated nitriles, unsaturated ethers, acrylated urethanes and unsaturated polyesters and mixtures thereof.

Most preferably the monomer of component (a) is styrene, butadiene, vinyl chloride, acrylic acid, methacrylic acid, vinyl acetate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, trimethylolpropane triacrylate, polyethylene glycol diacrylate or methyl methacrylate.
45

Still more preferably the monomer is styrene, butadiene, acrylic acid or methacrylic acid.

The compositions of the instant invention may also contain additional inhibitors, such as hydroquinone, the monomethyl ether of hydroquinone, (these often being required by monomer specifications) or catechol, tert-butylated hydroquinones or catechols, other alkylated phenols, nitrosophenols and nitrosophenylhydroxylamines.
50

The inhibited compositions may also contain metal deactivators and UV absorbers to improve light stability; or stabilizers such as amines to retard acid-catalyzed degradation; or thermal or photoinitiators; and other conventional additives.

55 The instant invention also pertains to a process for preventing the premature polymerization of a monomer polymerizable by free radical initiation which comprises adding to said monomer (a) an effective amount of a combination of compounds of any of the components (b) described above. The process of the instant invention involves simply dissolving an effective inhibiting amount of the inhibitor in the monomer prior to exposure of the latter to conditions where the premature, undesired free radical initiated polymerization might occur.

Preferably, this process comprises adding 50 to 10,000 of a mixture of components (i) and (ii) in a weight ratio of from 1:10 to 1000:1 to a continuous fluid feed stream to deactivate the autocatalytic polymerization, in any part of the continuous process equipment, such as reactor, reboiler, distillation column, etc., of any ethylenically unsaturated monomer present in the feed stream, and further adding to said feed stream an additional 10 ppm to 500 ppm of said mixture as a makeup additive to maintain the desired concentration of said mixture in the fluid feed stream being processed.

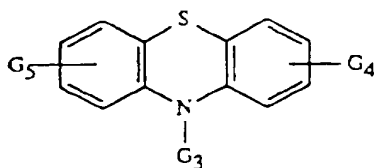
Preferably, this process is also carried out to prevent the fouling of processing equipment including reactors, pipes, stills, distillation columns, cracking towers and heat transfer surfaces during the processing of a monomer polymerizable by free radical initiation.

Still another aspect of the instant invention pertains to a monomer composition stabilized against premature polymerization, which comprises

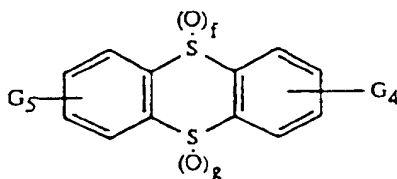
(a) an ethylenically unsaturated monomer or mixture of monomers, polymerizable by free radical initiation, and

(b) an effective amount, sufficient to inhibit premature polymerization of component (a), of a combination of

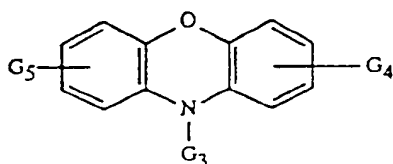
(i) a heterocyclic compound selected from any of formulas A to D



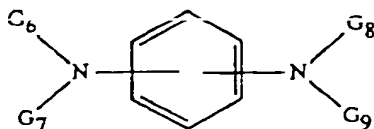
(A)



(B)



(C)



(D)

where

G₃ is hydrogen, alkyl of 1 to 4 carbon atoms or alkenyl of 3 to 4 carbon atoms,

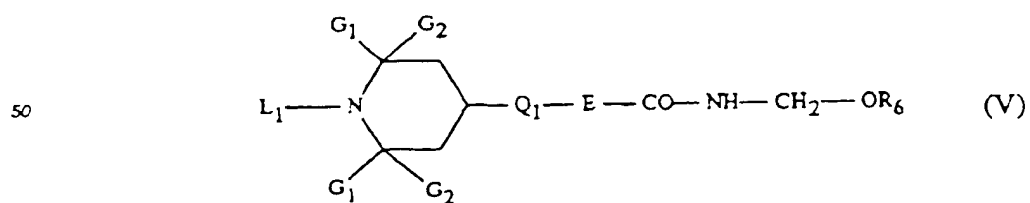
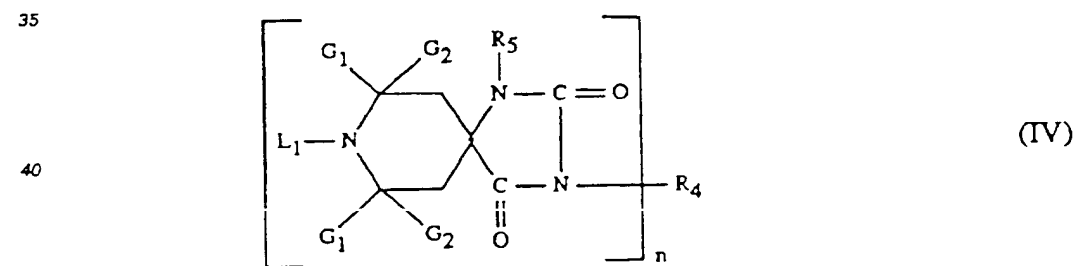
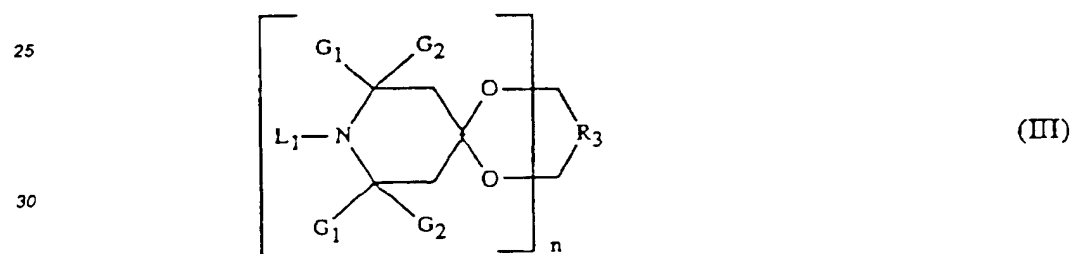
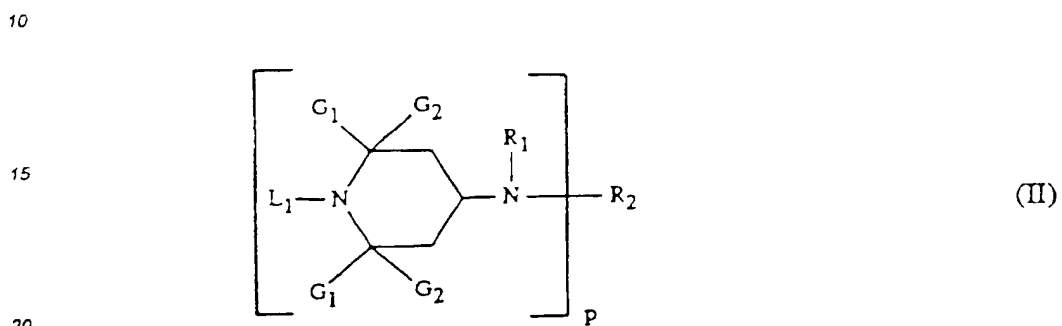
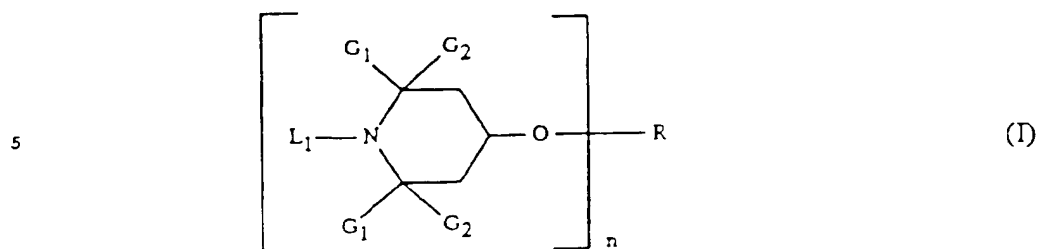
G₄ and G₅ are independently hydrogen or alkyl of 1 to 8 carbon atoms,

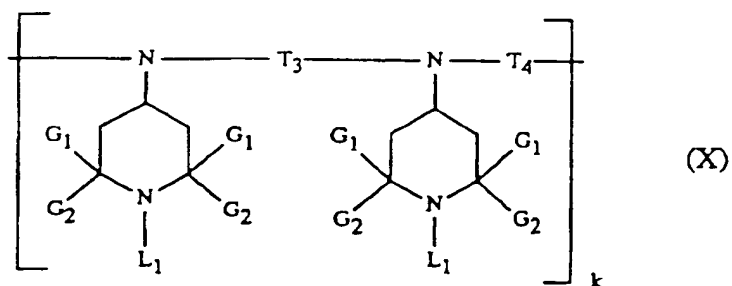
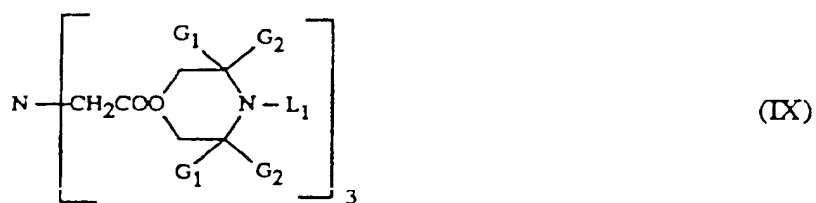
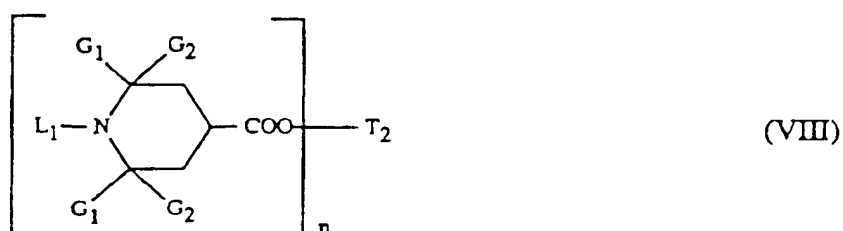
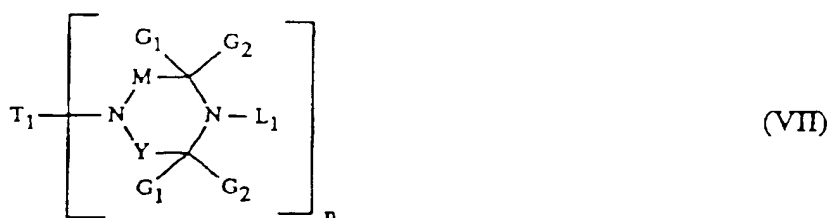
G₆ is aryl of 6 to 10 carbon atoms or aralkyl of 7 to 15 carbon atoms, and

G₇, G₈ and G₉ are independently hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms or alkaryl of 7 to 15 carbon atoms;

f and g are independently 0, 1 or 2, and

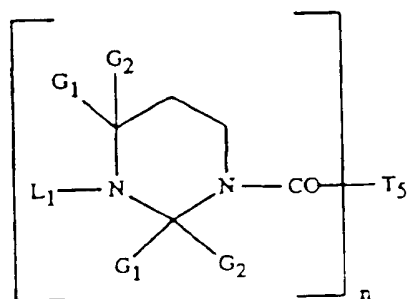
(ii) a compound or mixture of compounds of any of formulas I to XIX





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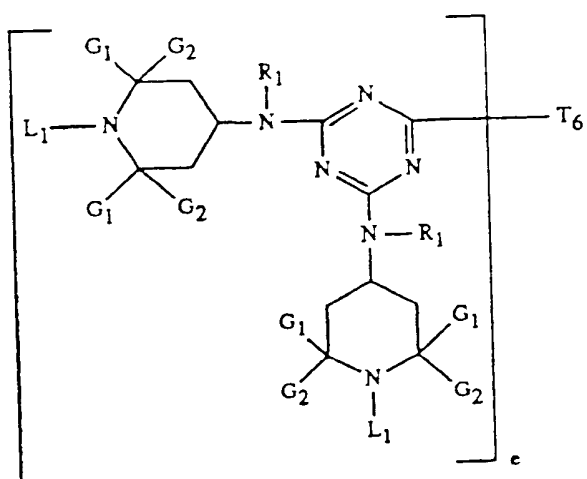
(XI)

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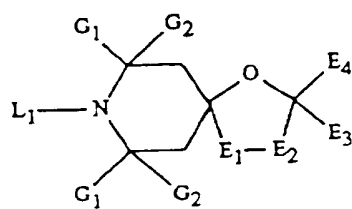
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(XII)

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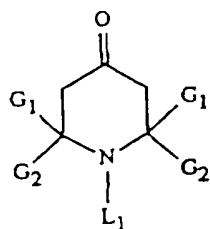
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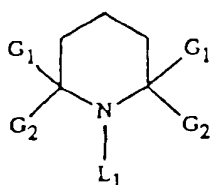
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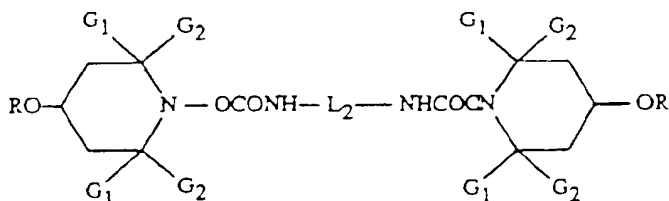


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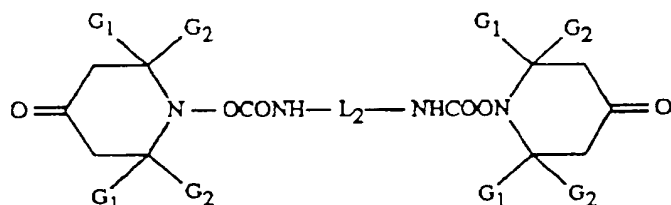
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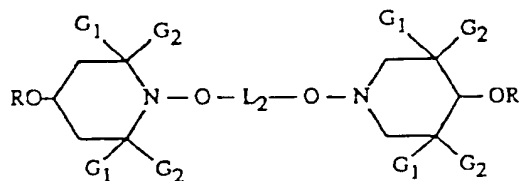
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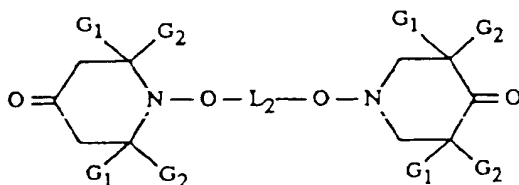
XVI



XVII



XVIII



XIX

wherein

G₁ and G₂ are independently alkyl of 1 to 4 carbon atoms;

L₁ is hydrogen, hydroxyl, alkyl of 1 to 18 carbon atoms, said alkyl substituted by hydroxyl, cyanoethyl, glycidyl, aralkyl of 7 to 15 carbon atoms or a monovalent acyl radical of an aliphatic, cycloaliphatic, araliphatic or aromatic acid, -OCONHL₃ or -OL₄,

where

L₃ is hydrogen, alkyl of 2 to 18 carbon atoms, allyl, cyclohexyl, aryl of 6 to 10 carbon atoms, said aryl substituted by one or two alkyl groups of 1 to 4 carbon atoms or is benzyl,

L₄ is alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, alkenyl of 2 to 18 carbon atoms, cycloalkenyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, a radical of a saturated or unsaturated bicyclic or tricyclic hydrocarbon of 7 to 12 carbon atoms or aryl of 6 to 10 carbon atoms or said aryl substituted by alkyl of 1 to 4 carbon atoms, or L₄ is -CH₂CH₂COOL₅ where L₅ is alkyl of 1 to 18 carbon atoms, n is 1 or 2,

when n is 1,

R is hydrogen, C₁-C₁₈-alkyl optionally interrupted by one or more oxygen atoms, cyanoethyl, benzyl, glycidyl, a monovalent acyl radical of an aliphatic, cycloaliphatic, araliphatic or aromatic acid, or of carbamic acid or of a phosphorus-containing acid, or a monovalent silyl radical; or

5 when n is 2,

R is C₁-C₁₂-alkylene, C₄-C₁₂-alkenylene, xylylene, a divalent acyl radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid, or of a dicarbamic acid or of a phosphorus-containing acid, or a bivalent silyl radical;

p is 1, 2 or 3,

10 R₁ is C₁-C₁₂-alkyl, C₅-C₇-cycloalkyl, C₇-C₈-aralkyl, C₂-C₁₈-alkanoyl, C₃-C₅-alkenoyl or benzoyl;

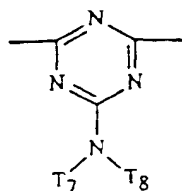
when p is 1,

R₂ is C₁-C₁₈-alkyl, C₅-C₇-cycloalkyl, C₂-C₈-alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula -CH₂CH(OH)-Z or of the formula -CONH-Z wherein Z is hydrogen, methyl or phenyl; or

15 when p is 2,

R₂ is C₂-C₁₂-alkylene, C₆-C₁₂-arylene, xylylene, a -CH₂CH(OH)CH₂-O-X-O-CH₂CH(OH)CH₂- wherein X is C₂-C₁₀-alkylene, C₆-C₁₅-arylene or C₆-C₁₂-cycloalkylene, or, provided that R₁ is not alkanoyl, alkenoyl or benzoyl, R₂ can also be a divalent acyl radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid, or can be the group -CO-; or R₁ and R₂ together when p is 1 can be the cyclic acyl radical of an aliphatic or aromatic 1,2- or 1,3-dicarboxylic acid; or

20 R₂ is



30

where T₇ and T₈ are independently hydrogen, alkyl of 1 to 18 carbon atoms, or T₇ and T₈ together are alkylene of 4 to 6 carbon atoms or 3-oxapentamethylene;

when p is 3,

35 R₂ is 2,4,6-triazinyl;

when n is 1,

R₃ is C₂-C₈-alkylene or hydroxyalkylene or C₄-C₂₂-acyloxyalkylene; or

when n is 2,

R₃ is (-CH₂)₂C(CH₂)₂;

40 when n is 1,

R₄ is hydrogen, C₁-C₁₂-alkyl, C₃-C₅-alkenyl, C₇-C₉-aralkyl, C₅-C₇-cycloalkyl, C₂-C₄-hydroxyalkyl, C₂-C₆-alkoxyalkyl, C₆-C₁₀-aryl, glycidyl, a group of formula -(CH₂)_m-COO-Q or of the formula -(CH₂)_m-O-CO-Q wherein m is 1 or 2 and Q is C₁-C₄-alkyl or phenyl; or

when n is 2,

45 R₄ is C₂-C₁₂-alkylene, C₆-C₁₂-arylene, a group -CH₂CH(OH)CH₂-O-X-O-CH₂CH(OH)CH₂- wherein X is C₂-C₁₀-alkylene, C₆-C₁₅-arylene or C₆-C₁₂-cycloalkylene, or a group -CH₂CH(OZ₁)CH₂-(OCH₂CH(OZ₁)CH₂)₂- wherein Z₁ is hydrogen, C₁-C₁₈-alkyl, allyl, benzyl, C₂-C₁₂-alkanoyl or benzoyl;

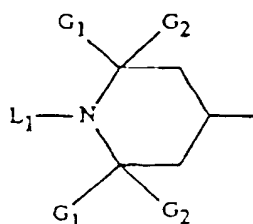
R₅ is hydrogen, C₁-C₁₂-alkyl, allyl, benzyl, glycidyl or C₂-C₆-alkoxyalkyl;

Q₁ is -N(R₇)- or -O-;

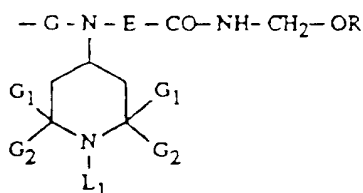
50 E is C₁-C₃-alkylene, the group -CH₂CH(R₈)-O- wherein R₈ is hydrogen, methyl or phenyl, the group -(CH₂)₃-NH- or a direct bond;

R₇ is C₁-C₁₈-alkyl, C₅-C₇-cycloalkyl, C₇-C₁₂-aralkyl, cyanoethyl, C₆-C₁₀-aryl, the group -CH₂CH(R₈)-OH; or a group of the formula

55



or a group of the formula



wherein G is C₂-C₆-alkylene or C₆-C₁₂-arylene; or
 R₇ is a group -E-CO-NH-CH₂-OR₈;
 R₈ is hydrogen or C₁-C₁₈-alkyl;

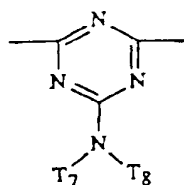
Formula VI denotes a recurring structural unit of a polymer where T is ethylene or 1,2-propylene, or is a repeating structural unit derived from an α -olefin copolymer with an alkyl acrylate or methacrylate;
 k is 2 to 100;

T₁ has the same meaning as R₂ when p is 1 or 2;

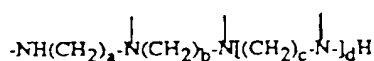
M and Y are independently methylene or carbonyl;

T₂ has the same meaning as R₄, and T₂ is octamethylene;

T₃ and T₄ are independently alkylene of 2 to 12 carbon atoms, of T₄ is



T₆ is



where a, b and c are independently 2 or 3, and d is 0 or 1;

e is 3 or 4;

T₅ is the same as R with the proviso that T₅ cannot be hydrogen when n is 1;

E₁ and E₂ being different, are each oxo or imino;

E₃ is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl, said phenyl or said naphthyl substituted by chlorine or by alkyl of 1 to 4 carbon atoms, or phenylalkyl of 7 to 12 carbon atoms, or said phenylalkyl substituted by alkyl of 1 to 4 carbon atoms; and

E₄ is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl or phenylalkyl of 7 to 12 carbon atoms; or

E₃ and E₄ together are polymethylene of 4 to 17 carbon atoms, or said polymethylene substituted by up to four alkyl groups of 1 to 4 carbon atoms;

L_2 is a divalent radical from an aliphatic, cycloaliphatic or aromatic diisocyanate from which the two -NCO groups are removed, or is an alkanediyl of 1 to 18 carbon atoms or cyclohexanediyl.

The monomers of component (a) of this invention are any having at least one carbon-carbon double bond capable of undergoing free radical induced polymerization. Such monomers are well known in commerce and comprise a wide variety of structural types. Typical examples of such monomers are the olefinic hydrocarbons such as styrene, α -methylstyrene and divinylbenzene; dienes such as butadiene and isoprene; halogenated monomers such as vinyl chloride, chloroprene, vinylidene chloride, vinylidene fluoride and vinyl fluoride; unsaturated acids such as acrylic acid, methacrylic acid and crotonic acid; unsaturated esters such as vinyl acetate, alkyl acrylates and alkyl methacrylates such as methyl methacrylate, ethyl acrylate, methyl acrylate, 2-hydroxyethyl acrylate and methacrylate, ethylene bismethacrylate, trimethylolpropane triacrylate, acrylated epoxy resin and polyethylene glycol diacrylate; unsaturated amides such as acrylamide, N,N-dimethylacrylamide, methylene-bisacrylamide and N-vinylpyrrolidone; unsaturated nitrile monomers such as acrylonitrile; and unsaturated ethers such as methyl vinyl ether, and miscellaneous monomers such as the vinyl pyridines, diethyl vinylphosphonate and sodium styrenesulfonate.

The instant invention also pertains to the use of mixtures of said monomers and to the use of resins such as acrylate-terminated polyurethanes and unsaturated polyesters. The common feature making all of these materials relevant to the present invention is the presence of a polymerizable double bond.

Also in the category of monomers are unsaturated oils such as drying oils like linseed oil, where polymerization also incorporates oxygen. There are also adventitious monomers formed in refining processes, for example polymerizable olefinic unsaturation in gasoline, jet fuel, solvents, crude oil and cracked hydrocarbon streams. The common feature of all of these substances is encompassed in the broad term "monomers" and all are contemplated to be within the scope of instant component (a). Polymerization of such materials is often accompanied by autooxidation.

The acrylates, particularly acrylic acid itself, are unusually difficult to inhibit because of their inherent high polymerizability. The instant compounds are shown to be particularly effective in inhibiting acrylic acid from premature polymerization.

Preferably component (a) is a monomer selected from the group consisting of the olefinic hydrocarbons, dienes, halogenated monomers, unsaturated acids, unsaturated esters, unsaturated amides, unsaturated nitriles, unsaturated ethers, acrylated urethanes and unsaturated polyesters and mixtures thereof.

Most preferably the monomer of component (a) is styrene, butadiene, vinyl chloride, acrylic acid, methacrylic acid, vinyl acetate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, trimethylolpropane triacrylate, polyethylene glycol diacrylate or methyl methacrylate.

Still more preferably the monomer is styrene, butadiene, acrylic acid or methacrylic acid.

The N-hydrocarbyloxy derivatives useful in the instant invention are denoted by the various structures of formulas I to XV, where I and XV are preferred. Another group of preferred derivatives are 1-[2-(methoxycarbonyl)ethoxy]-4-benzyloxy-2,2,6,6-tetramethyl piperidine; 1-methoxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate; bis[1-(2-(methoxycarbonyl)ethoxy)-2,2,6,6-tetramethylpiperidin-4-yl] phthalate; 1-tert-butoxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate; 4-hydroxy-1-octyloxy-2,2,6,6-tetramethylpiperidine; 1-[2-(methoxycarbonyl)ethoxy]-2,2,6,6-tetramethylpiperidine; 1-methylcyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate; 4-benzyloxy-1-ethoxy-2,2,6,6-tetramethylpiperidine; 1-carbamoyloxy-4-benzoyloxy-2,2,6,6-tetramethylpiperidine; 4-hydroxy-1,2,2,6,6-pentamethylpiperidine; 1-butylcarbamoyloxy-4-benzoyloxy-2,2,6,6-tetramethylpiperidine; 1- α -methylbenzyloxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate; 1,4-dimethoxy-2,2,6,6-tetramethylpiperidine; bis[1-(2-(methoxycarbonyl)ethoxy)-2,2,6,6-tetramethylpiperidin-4-yloxy]-p-xylylene; 1-hydroxy-2,2,6,6-piperidin-4-yl benzoate; 4-hydroxy-1-methoxy-2,2,6,6-tetramethylpiperidine; 1-methoxy-2,2,6,6-tetramethylpiperidin-4-one; 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-one; 4-hydroxyethoxy-2,2,6,6-tetramethylpiperidine; bis(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate; and bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate. A preferred component (i) is of formula (A) and is preferably phenothiazine. Most of these N-hydrocarbyloxy derivatives are known compounds. The instant N-hydrocarbyloxy derivatives can be easily prepared from the corresponding hindered amines which are known

or which can be made by known procedures.

The instant N-hydrocarbyloxy derivatives are made by reacting a hydroxylamine with an alkyl halide or benzyl halide or reacting the hydroxylamine with an alkyl in presence of potassium butoxide.

Another method involves the preparation of the N-hydrocarbyloxy compounds directly from the hindered amine precursors using aqueous tert-butyl hydroperoxide, molybdenum trioxide in an appropriate hydrocarbon medium.

If any of the substituents in the above formulae are C₁-C₁₂-alkyl, they are for example methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-amyl, tert-amyl, n-hexyl, n-octyl, 2-ethylhexyl, tert-octyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl. As C₁-C₁₈-alkyl, R can be the aforementioned groups, and in addition for example n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

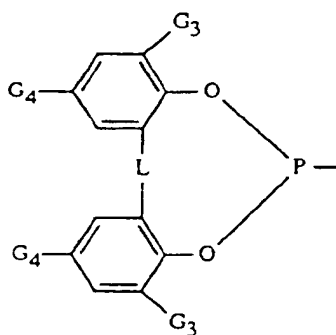
L₁ is particularly hydrogen, hydroxyl, alkyl of 1 to 12 carbon atoms, -OCONHL₃ where L₃ is hydrogen, alkyl of 2 to 8 carbon atoms or phenyl, or -OL₄ where L₄ is particularly alkyl of 1 to 12 carbon atoms, cycloalkyl of 5 to 8 carbon atoms or is -CH₂CH₂COOL₅ where L₅ is particularly alkyl of 1 to 12 carbon atoms.

If R is a monovalent acyl radical of a carboxylic acid, it is for example an acyl radical of acetic acid, stearic acid, salicylic acid, methacrylic acid, acrylic acid, maleic acid, benzoic acid, 2-ethylhexanoic acid or 3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid.

If R is a divalent acyl radical of a dicarboxylic acid, it is for example an acyl radical of adipic acid, succinic acid, suberic acid, sebacic acid, o-phthalic acid, butylmalonic acid, dibutylmalonic acid, dibenzylmalonic acid, 3,5-di-tert-butyl-4-hydroxybenzyl-butylmalonic acid or bicycloheptene dicarboxylic acid.

If R is a divalent acyl radical of a dicarbamic acid, it is for example an acyl radical of hexamethylenedicarbamic acid or 2,4-toluylenedicarbamic acid.

R is also an acyl radical of a phosphorus-containing acid of the formula



wherein L is a direct bond, methylene or alkylidene of 2 to 6 carbon atoms such as ethylidene, butylidene or amylidene. Preferably L is a direct bond, methylene or ethylidene.

G₃ and G₄ are independently alkyl of 1 to 4 carbon atoms, preferably methyl or tert-butyl. Most preferably G₃ and G₄ are each tert-butyl, or G₃ is tert-butyl and G₄ is methyl.

If any substituents are C₅-C₇-cycloalkyl, they are in particular cyclohexyl.

As C₇-C₈-aralkyl, R₁ is phenethyl and especially benzyl.

As C₂-C₁₈-alkanoyl, R₁ is for example propionyl, butyryl, octanoyl, lauroyl, hexadecanoyl, octadecanoyl, but especially acetyl; and as C₃-C₅-alkenoyl, R₁ is in particular acryloyl.

If R₂ is C₂-C₈-alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, it is for example 1-propenyl, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl, 2-octenyl, 2,2-dicyanovinyl, 1-methyl-2-cyano-2-methoxycarbonyl-vinyl or 2,2-diacetylaminovinyl.

When R₁ and R₂ are together a cyclic acyl radical, they are especially -CO-(CH₂)₅-.

If any substituents are C₂-C₁₂-alkylene, they are for example ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

If any substituents are C₆-C₁₅-arylene, they are for example o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

As C₆-C₁₂-cycloalkylene, X is especially cyclohexylene.

If R₃ is C₂-C₈-alkylene or hydroxyalkylene, it is for example ethylene, 1-methyl-ethylene, propylene, 2-ethylpropylene or 2-ethyl-2-hydroxymethylpropylene.

As C₄-C₂₂-acyloxyalkylene, R₃ is for example 2-ethyl-2-acetoxymethyl-propylene.

If any substituents are C₂-C₈-alkoxyalkyl, they are example methoxymethyl, ethoxymethyl, propoxymethyl, tert-butoxymethyl, ethoxyethyl, ethoxypropyl, n-butoxyethyl, tert-butoxyethyl, isopropoxyethyl or propoxyp-

ropyl.

If R_4 is C_3 - C_5 -alkenyl, it is for example 1-propenyl, allyl, methallyl, 2-butenyl or 2-pentenyl.

As C_7 - C_9 -aralkyl, R_4 is phenethyl or especially benzyl; and as C_5 - C_7 -cyclohexyl is especially cyclohexyl.

If R_4 is C_2 - C_4 -hydroxyalkyl, it is for example 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

As C_6 - C_{10} -aryl, R_4 is in particular phenyl or α - or β -naphthyl which is unsubstituted or substituted by halogen or C_1 - C_4 -alkyl.

If R_4 is C_2 - C_{12} -alkylene, it is for example ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

If R_4 is C_6 - C_{12} -arylene, it is for example *o*-, *m*- or *p*-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

If Z_1 is C_2 - C_{12} -alkanoyl, it is for example propionyl, butyryl, octanoyl, dodecanoyl or preferably acetyl.

As C_5 - C_7 -cycloalkyl, R_7 is particularly cyclohexyl.

As C_6 - C_{10} -aryl, R_7 is particularly phenyl or α - or β -naphthyl which is unsubstituted or substituted with halogen or C_1 - C_4 -alkyl.

As C_1 - C_3 -alkylene, E is for example methylene, ethylene or propylene.

As C_2 - C_6 -alkylene, G is for example ethylene, propylene, 2,2-dimethylpropylene, tetramethylene or hexamethylene; and as C_6 - C_{12} -arylene, G is *o*-, *m*- or *p*-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

Diisocyanates of the formula $L_2-(NCO)_2$ useful to form the compounds of formula XVI or XVII are aliphatic, cycloaliphatic or aromatic diisocyanates and are selected from the group consisting of ethylene diisocyanate, 1,2-diisocyanatopropane, 1,3-diisocyanatopropane, 1,6-diisocyanatohexane, 1,2-diisocyanatocyclohexane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatobenzene, bis(4-isocyanatocyclohexyl)methane, bis(4-isocyanatocyclohexenyl)methane, bis(4-isocyanato-phenyl)methane, 2,6- and 2,4-toluene diisocyanate, 3,3-dichloro-4,4'-diisocyanatobiphenyl, 1,5-diisocyanatonaphthalene, hydrogenated toluene diisocyanate, 1-isocyanato-5-isocyanato-1,3,3-trimethylcyclohexane (=isophorone diisocyanate), 2,2'-diisocyanatodiethyl fumate, 1,5-diisocyanato-1-carboxypentane, 1,2-, 1,3-, 1,6-, 1,7-, 2,7- and 2,3-diisocyanatonaphthalene, 2,4- and 2,7-diisocyanato-1-methylnaphthalene, 4,4'-diisocyanatobiphenyl, bis(4-isocyanatophenyl)ethane, bis(4-isocyanatophenyl) ether and 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate.

The preferred diisocyanates are isophorone diisocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and 2,4- and 2,6-toluene diisocyanate.

An effective inhibiting amount of an instant components (i) and (ii) of this invention needed to retard or prevent premature free radical induced polymerization of a monomer or monomer mixture is as follows: the weight ratio of component (i) to component (ii) is from 1:10 to 1000:1, preferably 1:1 to 10:1, and where the total concentration is in the range of 50-10,000 ppm, preferably 200-600 ppm, based on the monomer being stabilized. The lower amounts would be used where the degree of inhibition required is not great such as when the monomers are to be used promptly, or which will be stored refrigerated, or which are inherently less prone to polymerize readily such as monomers with internal double bonds. The higher amounts of inhibitor would be used where the monomer is to be stored for prolonged periods of time, especially under relatively warm conditions or where contamination is likely, or where exposure to photoinitiation is likely, or where the monomer is especially prone to rapid polymerization with little provocation such as with the acrylates and acrylic acid. Those skilled in the art of vinyl polymerization are well aware of the relative polymerizability of monomers and of their relative stabilities.

The stabilized compositions of this invention are distinguished by their lack of color.

The compositions of the instant invention may also contain additional inhibitors, such as hydroquinone, the monomethyl ether of hydroquinone, (these often being required by monomer specifications) or catechol, tert-butylated hydroquinones or catechols, other alkylated phenols, nitrosophenols and nitrosophenylhydroxylamines.

The inhibited compositions may also contain metal deactivators and UV absorbers to improve light stability; or stabilizers such as amines to retard acid-catalyzed degradation; or thermal or photoinitiators; and other conventional additives.

When it is desired to subject the inhibited monomer to polymerization, the inhibitor can either be removed or overridden by sufficient polymerization initiator. Removal can be accomplished by distillation, absorption or washing with an acidic solution. It is possible to remove the instant 1-hydroxy derivatives while leaving the phenolic antioxidants in the monomer by use of strong acid ion exchange resins. The polymerization inhibiting action of the instant compounds can be overridden by use of sufficient free radical initiator, actinic light irradiation, electron beam exposure or other polymerization initiating means.

The instant invention also pertains to a process for preventing the premature polymerization of a monomer polymerizable by free radical initiation which comprises adding to said monomer (a) an effective amount of a combination of compounds of any of the components (b) described above. The process of the instant invention

involves simply dissolving an effective inhibiting amount of the inhibitor in the monomer prior to exposure of the latter to conditions where the premature, undesired free radical initiated polymerization might occur.

Preferably, this process comprises adding 50 to 10,000 of a mixture of components (i) and (ii) in a weight ratio of from 1:10 to 1000:1 to a continuous fluid feed stream to deactivate the autocatalytic polymerization, in any part of the continuous process equipment, such as reactor, reboiler, distillation column, etc., of any ethylenically unsaturated monomer present in the feed stream, and further adding to said feed stream an additional 10 ppm to 500 ppm of said mixture as a makeup additive to maintain the desired concentration of said mixture in the fluid feed stream being processed.

Preferably, this process is also carried out to prevent the fouling of processing equipment including reactors, pipes, stills, distillation columns, cracking towers and heat transfer surfaces during the processing of a monomer polymerizable by free radical initiation.

The following examples are presented for the purpose of illustration only and are not to be construed as limiting the instant invention in any manner whatsoever.

The apparatus used in the following experiments is fabricated from an 80 mm OD and 3 mm thick glass tubing, 14 inches (35.6 cm) high, closed on one end and flared at the other end to fit a resin kettle top. The kettle is equipped with a water condenser and nitrogen inlet tube. Except where noted, the polymer reported in the examples is formed in the vapor phase (refluxing) region on the walls of the apparatus about 3 inches (7.6cm) above the surface of the liquid monomer.

Example 1:

To demonstrate the need for a pot stabilizer, an experiment is run without any stabilizing additive in the acrylic acid monomer. A dry resin kettle is weighed and the weight recorded. A 100 ml (105 g) aliquot of acrylic acid is charged into the kettle and flushed with dry nitrogen flowing at 250 ml/min for 15 minutes. The kettle is then immersed in an oil bath containing approximately 6 liters of oil such that the surface of the acrylic acid in the kettle is about 2 inches (5.1 cm) below the level of the oil in the bath. The oil bath is heated to 150°C and the acrylic acid is refluxed for 70 minutes. After approximately 15 minutes, the monomer begins to gel and white insoluble polymer is observed to grow in the monomer liquid. Only a small amount of acrylic acid monomer remains after 70 minutes. The kettle is removed from the oil bath and wiped free of oil. The resulting white polymer is rinsed with hexane to remove residual monomer, dried and weighed to determine the total amount of polymeric material collected inside the kettle. Some 82.9 g of white polymer is obtained. The resin kettle cannot be used for any further experiments.

Examples 2-24:

Following the general procedure of Example 1, 100 ml (105 g) of acrylic acid refluxed for 70 minutes in the presence of the stabilizers indicated and the amount of polymer obtained is a measure of the relative effectiveness of the stabilizers used. The lesser is the amount of polymer formed, the more effective is the stabilizer used. The results are given in the table below.

Example	Additive* (100 ppm)	Pot Stabilizer (1000 ppm)	Polymer Obtained (grams)
5	2	A	phenothiazine
	3	B	phenothiazine
	4	C	phenothiazine
10	5	D	phenothiazine
	6	E	phenothiazine
	7	F	phenothiazine
15	8	G	phenothiazine
	9	H	phenothiazine
	10	I	phenothiazine
20	11	J	phenothiazine
	12	K	phenothiazine
	13	L	phenothiazine
25	14	M	phenothiazine
	15	N	phenothiazine
	16	O	phenothiazine
30	17	P	phenothiazine
	18	Q	phenothiazine
	19	R	phenothiazine
35	20	S	phenothiazine
	21	T	phenothiazine
	11	U	phenothiazine
40	23	V	phenothiazine
	24	W	phenothiazine

*A is N,N-diethylhydroxylamine.

B is 1-[2-(methoxycarbonyl)ethoxy]-4-benzyloxy-2,2,6,6-tetramethyl piperidine.

C is 1-methoxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate.

D is bis[1-(2-(methoxycarbonyl)ethoxy)-2,2,6,6-tetramethylpiperidin-4-yl] phthalate.

E is 1-tert-butoxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate.

F is 4-hydroxy-1-octyloxy-2,2,6,6-tetramethylpiperidine.

G is 1-[2-(methoxycarbonyl)ethoxy]-2,2,6,6-tetramethylpiperidine.

H is 1-methylcyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate.

I is 4-benzyloxy-1-ethoxy-2,2,6,6-tetramethylpiperidine.

J is 1-carbamoyloxy-4-benzoyloxy-2,2,6,6-tetramethylpiperidine.

K is 4-hydroxy-1,2,2,6,6-pentamethylpiperidine.

L is 1-butylcarbamoyloxy-4-benzoyloxy-2,2,6,6-tetramethylpiperidine.

M is 1- α -methylbenzyloxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate.

N is 1,4-dimethoxy-2,2,6,6-tetramethylpiperidine.

O is bis[1-(2-(methoxycarbonyl)ethoxy)-2,2,6,6-tetramethylpiperidin-4-yloxy]-p-xylylene.

P is N,N-di-tert-butylhydroxylamine.

Q is 1-hydroxy-2,2,6,6-piperidin-4-yl benzoate.

R is 4-hydroxy-1-methoxy-2,2,6,6-tetramethylpiperidine.

S is 1-methoxy-2,2,6,6-tetramethylpiperidin-4-one.

T is 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-one.

U is 4-hydroxyethoxy-2,2,6,6-tetramethylpiperidine.

V is bis(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

W is bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

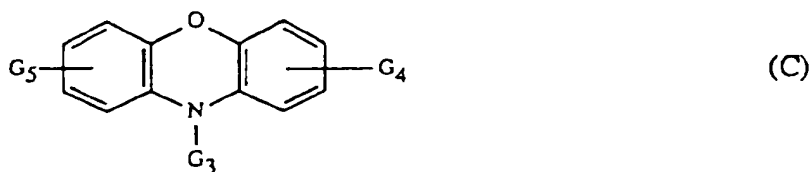
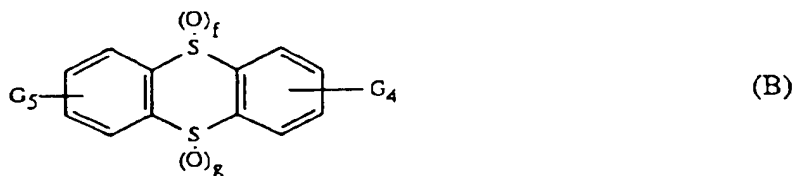
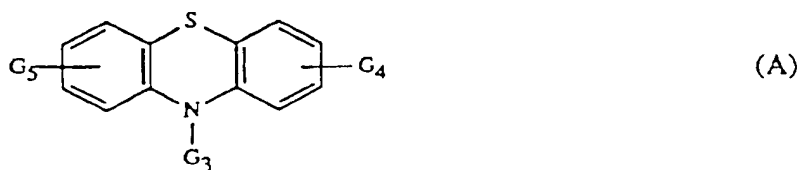
Examples 25-27:

When using the procedure of Example 2, the acrylic acid is replaced respectively with the monomers shown below, no polymer is formed in the presence of 100 ppm of 1-tert-butoxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate and 1000 ppm of phenothiazine.

Example	Monomer
25	methyl methacrylate
26	2-hydroxyethyl methacrylate
27	2-hydroxyethyl acrylate

Claims

1. A monomer composition, stabilized against premature polymerization, which comprises
 - (a) an ethylenically unsaturated monomer or mixture of monomers, polymerizable by free radical initiation, and
 - (b) an effective amount, sufficient to inhibit the premature polymerization of component (a), which is a combination of
 - (i) a heterocyclic compound selected from any of formulas A to C



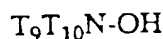
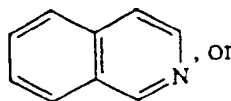
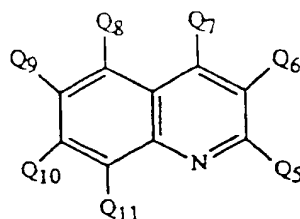
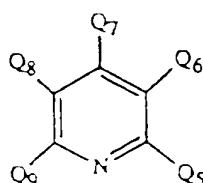
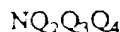
where

G_3 is hydrogen, alkyl of 1 to 4 carbon atoms or alkenyl of 3 to 4 carbon atoms,

G_4 and G_5 are independently hydrogen or alkyl of 1 to 8 carbon atoms, and

f and g are independently 0, 1 or 2, and

(ii) a primary, secondary or tertiary amine, or hydroxylamine, or mixture thereof, of the formula



wherein

Q_2 , Q_3 and Q_4 are independently hydrogen, alkyl of 1 to 18 carbon atoms, said alkyl substituted by hydroxy, alkenyl of 3 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by alkyl of 1 to 12 carbon atoms or by phenyl, with the proviso that all of Q_2 , Q_3 and Q_4 are not hydrogen, cycloalkyl, phenylalkyl or aryl at the same time;

or

Q_3 and Q_4 together are straight or branched alkylene of 4 to 8 carbon atoms, 3-oxapentamethylene, 3-thiapentamethylene, 3-iminopentamethylene or 3-methyliminopentamethylene, and

Q_2 is hydrogen or alkyl of 1 to 8 carbon atoms;

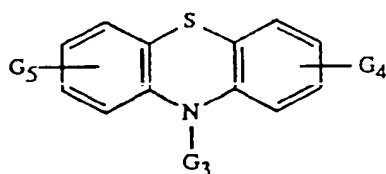
Q_5 , Q_6 , Q_7 , Q_8 , Q_9 , Q_{10} and Q_{11} are independently hydrogen, methyl or ethyl; or

T_9 is hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms or phenylalkyl of 7 to 15 carbon atoms, and

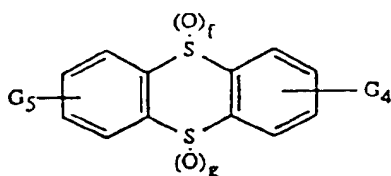
T_{10} is alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms or phenylalkyl of 7 to 15 carbon atoms.

2. A composition according to claim 1 wherein the effective amount is a combination of component (i) and component (ii) in a weight ratio of (i):(ii) of 1:10 to 1000:1, preferably 1:1 to 10:1, and where the total concentration of (i) plus (ii) is in the range of 50-10,000 ppm, preferably 200-600 ppm, based on the monomer being stabilized.
3. A composition according to claim 1 wherein component (a) is a monomer selected from the group consisting of the olefinic hydrocarbons, dienes, halogenated monomers, unsaturated acids, unsaturated esters, unsaturated amides, unsaturated nitriles, unsaturated ethers, acrylated urethanes and unsaturated polyesters and mixtures thereof.

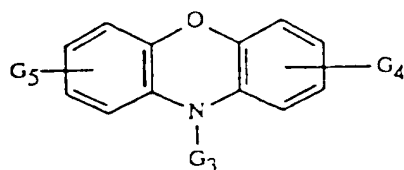
4. A composition according to claim 4 wherein the monomer is styrene, butadiene, vinyl chloride, acrylic acid, methacrylic acid, vinyl acetate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, trimethylolpropane triacrylate, polyethylene glycol diacrylate or methyl methacrylate, preferably styrene, butadiene, acrylic acid or methacrylic acid.
5. A composition according to claim 1 wherein component (i) is phenothiazine.
6. A composition according to claim 1 wherein component (ii) is N,N-diethylhydroxylamine or N,N-di-tert-butylhydroxylamine.
7. A composition according to claim 1 which additionally contains another stabilizer selected from the group consisting of hydroquinone and monomethyl ether of hydroquinone.
8. A process for preventing the premature polymerization of a monomer polymerizable by free radical initiation which comprises
 adding to said monomer (a) an effective amount of a combination of compounds of component (b) according to claim 1.
9. A process according to claim 8 for preventing the fouling of processing equipment including reactors, pipes, stills, distillation columns, cracking towers and heat transfer surfaces during the processing of a monomer polymerizable by free radical initiation which comprises
 adding to said monomer (a), before processing is begun, an effective amount of a combination of compounds of component (b) according to claim 1.
10. A process according to claim 8 which comprises
 adding 50 to 10,000 ppm of component (b), according to claim 1, in a weight ratio of from 1:10 to 1000:1, to a continuous feed stream to deactivate the autocatalytic polymerization, in any part of the continuous process equipment, of any ethylenically unsaturated monomer present in the feed stream, and
 further adding to said feed stream an additional 10 ppm to 500 ppm of said mixture as a makeup additive to maintain the desired concentration of said mixture in the fluid feed stream being processed.
11. A monomer composition, stabilized against premature polymerization, which comprises
 (a) an ethylenically unsaturated monomer or mixture of monomers, polymerizable by free radical initiation, and
 (b) an effective amount, sufficient to inhibit premature polymerization of component (a), of a combination of
 (i) a heterocyclic compound selected from any of formulas A to D



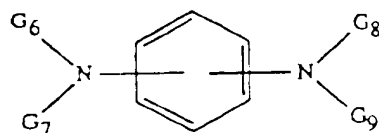
(A)



(B)



(C)



(D)

where

G_3 is hydrogen, alkyl of 1 to 4 carbon atoms or alkenyl of 3 to 4 carbon atoms,

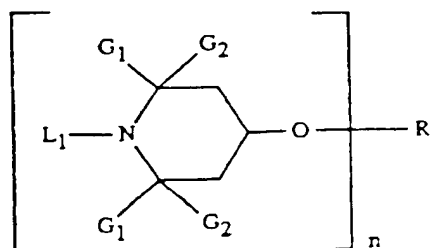
G_4 and G_5 are independently hydrogen or alkyl of 1 to 8 carbon atoms,

G_6 is aryl of 6 to 10 carbon atoms or aralkyl of 7 to 15 carbon atoms, and

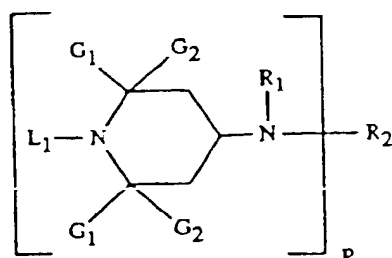
G_7 , G_8 and G_9 are independently hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms or alkaryl of 7 to 15 carbon atoms;

f and g are independently 0, 1 or 2, and

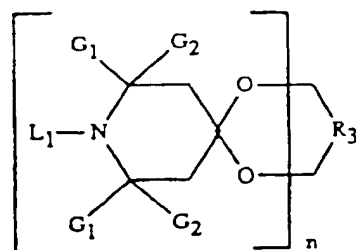
(ii) a compound or mixture of compounds of any of formulas I to XIX



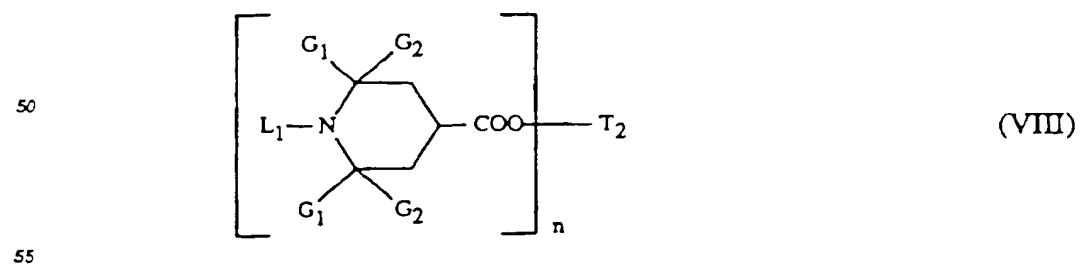
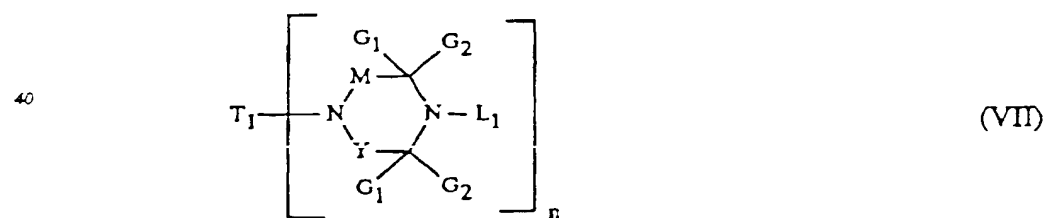
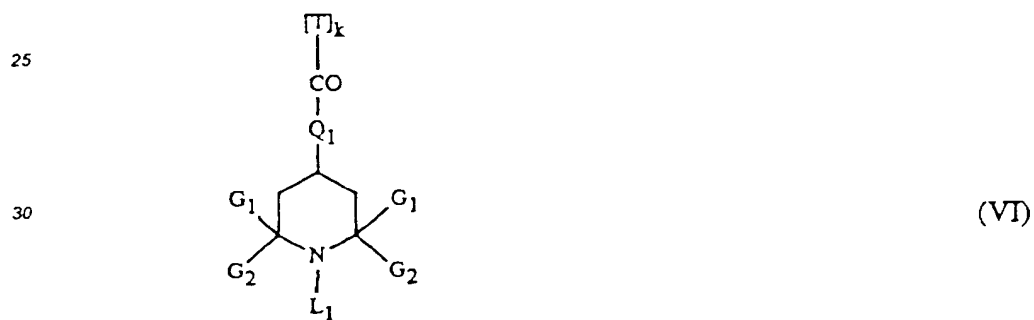
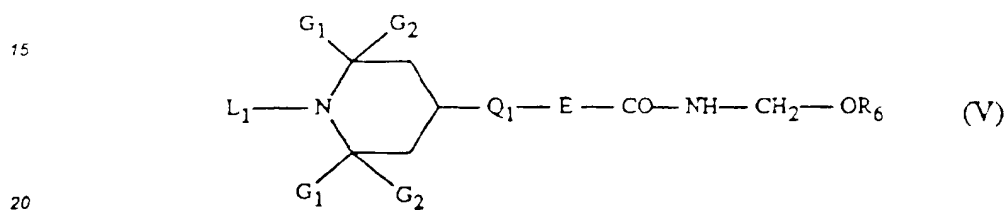
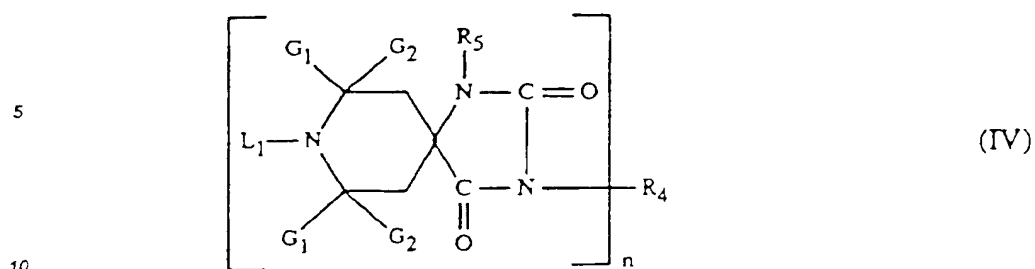
(I)

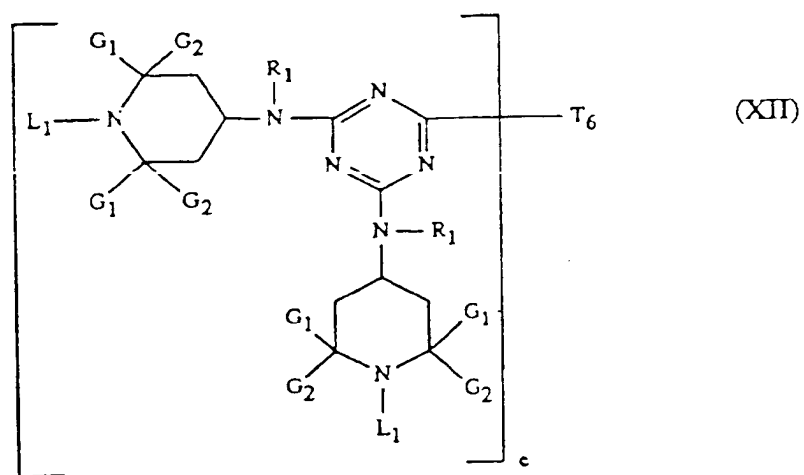
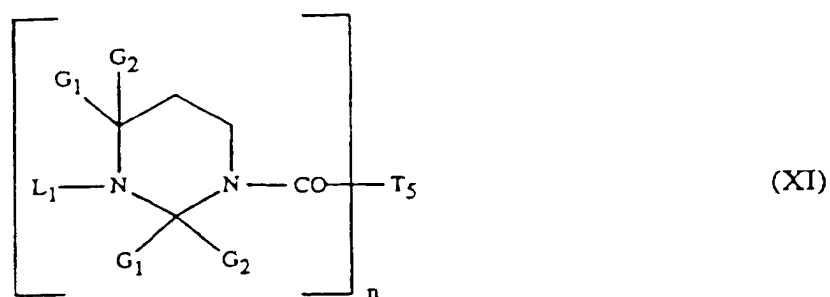
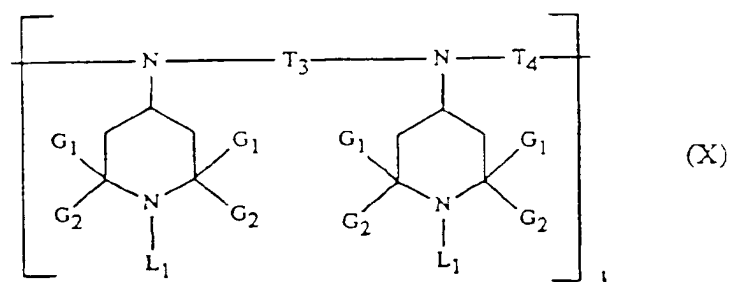
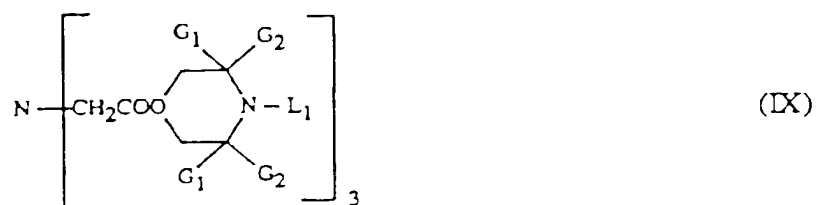


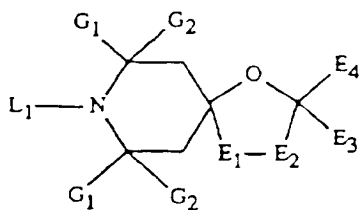
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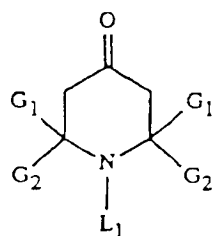
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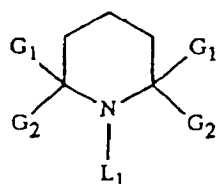




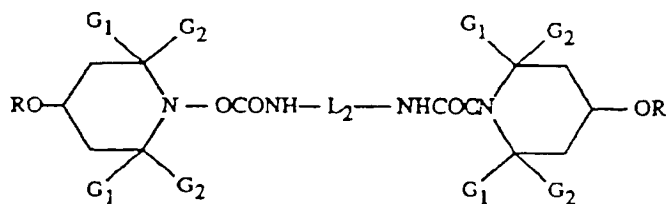
(XIII)



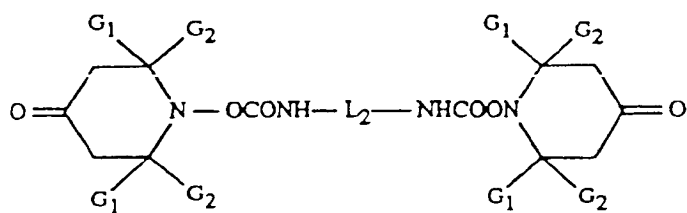
(XIV)



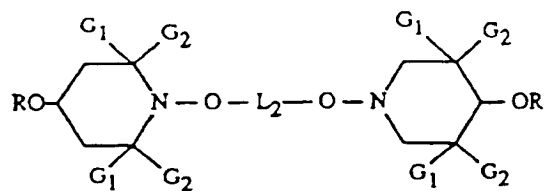
(XV)



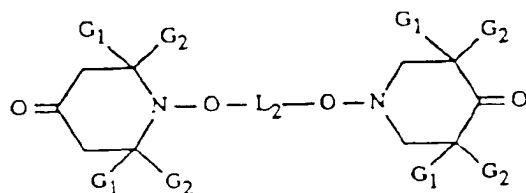
XVI



XVII



XVIII



XIX

wherein

G_1 and G_2 are independently alkyl of 1 to 4 carbon atoms;

L_1 is hydrogen, hydroxyl, alkyl of 1 to 18 carbon atoms, said alkyl substituted by hydroxyl, cyanoethyl, glycidyl, aralkyl of 7 to 15 carbon atoms or a monovalent acyl radical of an aliphatic, cycloaliphatic, araliphatic or aromatic acid, $-OCONHL_3$ or $-OL_4$, where

L_3 is hydrogen, alkyl of 2 to 18 carbon atoms, allyl, cyclohexyl, aryl of 6 to 10 carbon atoms, said aryl substituted by one or two alkyl groups of 1 to 4 carbon atoms or is benzyl,

L_4 is alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, alkenyl of 2 to 18 carbon atoms, cycloalkenyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, a radical of a saturated or unsaturated bicyclic or tricyclic hydrocarbon of 7 to 12 carbon atoms or aryl of 6 to 10 carbon atoms or said aryl substituted by alkyl of 1 to 4 carbon atoms, or L_4 is $-CH_2CH_2COOL_5$ where L_5 is alkyl of 1 to 18 carbon atoms, n is 1 or 2,

when n is 1,

R is hydrogen, C_1 - C_{18} -alkyl optionally interrupted by one or more oxygen atoms, cyanoethyl, benzyl, glycidyl, a monovalent acyl radical of an aliphatic, cycloaliphatic, araliphatic or aromatic acid, or of carbamic acid or of a phosphorus-containing acid, or a monovalent silyl radical; or

when n is 2,

R is C_1 - C_{12} -alkylene, C_4 - C_{12} -alkenylene, xylene, a divalent acyl radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid, or of a dicarbamic acid or of a phosphorus-containing acid, or a bivalent silyl radical;

p is 1, 2 or 3,

R_1 is C_1 - C_{12} -alkyl, C_5 - C_7 -cycloalkyl, C_7 - C_8 -aralkyl, C_2 - C_{18} -alkanoyl, C_3 - C_5 -alkenoyl or benzoyl;

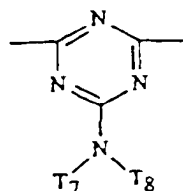
when p is 1,

R_2 is C_1 - C_{18} -alkyl, C_5 - C_7 -cycloalkyl, C_2 - C_8 -alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula $-CH_2CH(OH)-Z$ or of the formula $-CONH-Z$ wherein Z is hydrogen, methyl or phenyl; or

when p is 2,

R_2 is C_2 - C_{12} -alkylene, C_6 - C_{12} -arylene, xylene, a $-CH_2CH(OH)CH_2-O-X-O-CH_2CH(OH)CH_2-$ wherein X is C_2 - C_{10} -alkylene, C_6 - C_{15} -arylene or C_6 - C_{12} -cycloalkylene; or, provided that R_1 is not alkanoyl, alkenoyl or benzoyl, R_2 can also be a divalent acyl radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid, or can be the group $-CO-$; or R_1 and R_2 together when p is 1 can be the cyclic acyl radical of an aliphatic or aromatic 1,2- or 1,3-dicarboxylic acid; or

R_2 is



where T_7 and T_8 are independently hydrogen, alkyl of 1 to 18 carbon atoms, or T_7 and T_8 together are alkylene of 4 to 6 carbon atoms or 3-oxapentamethylene;

when p is 3,

R_2 is 2,4,6-triazinyl;

when n is 1,

R_3 is C_2 - C_8 -alkylene or hydroxyalkylene or C_4 - C_{22} -acyloxyalkylene; or

when n is 2,

R_3 is $(-CH_2)_2C(CH_2-)_2$;

when n is 1,

R_4 is hydrogen, C_1 - C_{12} -alkyl, C_3 - C_5 -alkenyl, C_7 - C_9 -aralkyl, C_5 - C_7 -cycloalkyl, C_2 - C_4 -hydroxyalkyl, C_2 - C_6 -alkoxyalkyl, C_6 - C_{10} -aryl, glycidyl, a group of formula $-(CH_2)_m-COO-Q$ or of the formula $-(CH_2)_m-O-CO-Q$ wherein m is 1 or 2 and Q is C_1 - C_4 -alkyl or phenyl; or

when n is 2,

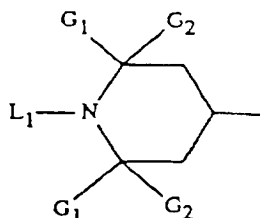
R_4 is C_2 - C_{12} -alkylene, C_6 - C_{12} -arylene, a group $-CH_2CH(OH)CH_2-O-X-O-CH_2CH(OH)CH_2-$ wherein X is C_2 - C_{10} -alkylene, C_6 - C_{15} -arylene or C_6 - C_{12} -cycloalkylene, or a group $-CH_2CH(OZ_1)CH_2-(OCH_2CH(OZ_1)CH_2)_2-$ wherein Z_1 is hydrogen, C_1 - C_{18} -alkyl, allyl, benzyl, C_2 - C_{12} -alkanoyl or benzoyl;

R_5 is hydrogen, C_1 - C_{12} -alkyl, allyl, benzyl, glycidyl or C_2 - C_6 -alkoxyalkyl;

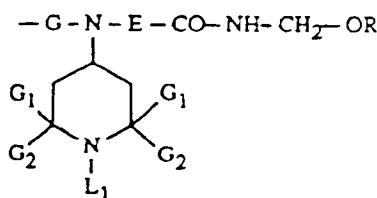
Q_1 is $-N(R_7)-$ or $-O-$;

E is C_1 - C_3 -alkylene, the group $-CH_2CH(R_8)-O-$ wherein R_8 is hydrogen, methyl or phenyl, the group $-(CH_2)_3-NH-$ or a direct bond;

R_7 is C_1 - C_{18} -alkyl, C_5 - C_7 -cycloalkyl, C_7 - C_{12} -aralkyl, cyanoethyl, C_6 - C_{10} -aryl, the group $-CH_2CH(R_8)-OH$; or a group of the formula



or a group of the formula



wherein G is C_2 - C_6 -alkylene or C_6 - C_{12} -arylene; or

R_7 is a group $-E-CO-NH-CH_2-OR_8$;

R_8 is hydrogen or C_1 - C_{18} -alkyl;

Formula VI denotes a recurring structural unit of a polymer where T is ethylene or 1,2-propylene, or is a repeating structural unit derived from an α -olefin copolymer with an alkyl acrylate or methacrylate;

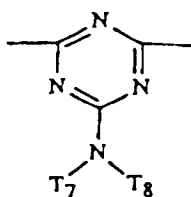
k is 2 to 100;

T_1 has the same meaning as R_2 when p is 1 or 2;

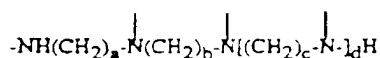
M and Y are independently methylene or carbonyl;

T_2 has the same meaning as R_4 , and T_2 is octamethylene;

T_3 and T_4 are independently alkylene of 2 to 12 carbon atoms, of T_4 is



T₆ is



where a, b and c are independently 2 or 3, and d is 0 or 1;

e is 3 or 4;

T₅ is the same as R with the proviso that T₅ cannot be hydrogen when n is 1;

E₁ and E₂, being different, are each oxo or imino;

E₃ is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl, said phenyl or said naphthyl substituted by chlorine or by alkyl of 1 to 4 carbon atoms, or phenylalkyl of 7 to 12 carbon atoms, or said phenylalkyl substituted by alkyl of 1 to 4 carbon atoms; and

E₄ is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl or phenylalkyl of 7 to 12 carbon atoms; or E₃ and E₄ together are polymethylene of 4 to 17 carbon atoms, or said polymethylene substituted by up to four alkyl groups of 1 to 4 carbon atoms;

L₂ is a divalent radical from an aliphatic, cycloaliphatic or aromatic diisocyanate from which the two -NCO groups are removed, or is an alkanediyl of 1 to 18 carbon atoms or cyclohexanediyl

12. A composition according to claim 11 wherein the effective amount is a combination of component (i) and component (ii) in a weight ratio of (i):(ii) of 1:10 to 1000:1, preferably 1:1 to 10:1, and where the total concentration of (i) plus (ii) is in the range of 50-10,000 ppm, preferably 200-600 ppm, preferably 200-600 ppm, based on the monomer being stabilized.
13. A composition according to claim 11 wherein component (a) is a monomer selected from the group consisting of the olefinic hydrocarbons, dienes, halogenated monomers, unsaturated acids, unsaturated esters, unsaturated amides, unsaturated nitriles, unsaturated ethers, acrylated urethanes and unsaturated polyesters and mixtures thereof.
14. A composition according to claim 13 wherein the monomer is styrene, butadiene, vinyl chloride, acrylic acid, methacrylic acid, vinyl acetate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, trimethylolpropane triacrylate, polyethylene glycol diacrylate or methyl methacrylate, preferably styrene, butadiene, acrylic acid or methacrylic acid.
15. A composition according to claim 11 wherein component (i) is phenothiazine.
16. A composition according to claim 11 wherein component (ii) is of formula I or XV, preferably of formula I.
17. A composition according to claim 11 wherein component (ii) is selected from the group consisting of 1-[2-(methoxycarbonyl)ethoxy]-4-benzyloxy-2,2,6,6-tetramethyl piperidine;
1-methoxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate;
bis[1-(2-(methoxycarbonyl)ethoxy)-2,2,6,6-tetramethylpiperidin-4-yl] phthalate;
1-tert-butoxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate;
4-hydroxy-1-octyloxy-2,2,6,6-tetramethylpiperidine;
1-[2-(methoxycarbonyl)ethoxy]-2,2,6,6-tetramethylpiperidine; 1-methylcyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate;
4-benzyloxy-1-ethoxy-2,2,6,6-tetramethylpiperidine;
1-carbamoyloxy-4-benzoyloxy-2,2,6,6-tetramethylpiperidine;
4-hydroxy-1,2,2,6,6-pentamethylpiperidine;
1-butylcarbamoyloxy-4-benzoyloxy-2,2,6,6-tetramethylpiperidine;
1- α -methylbenzyloxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate;
1,4-dimethoxy-2,2,6,6-tetramethylpiperidine;
bis[1-(2-(methoxycarbonyl)ethoxy)-2,2,6,6-tetramethylpiperidin-4-yl]oxy-p-xylylene;
1-hydroxy-2,2,6,6-piperidin-4-yl benzoate;
4-hydroxy-1-methoxy-2,2,6,6-tetramethylpiperidine;
1-methoxy-2,2,6,6-tetramethylpiperidin-4-one;
1-hydroxy-2,2,6,6-tetramethylpiperidin-4-one;

4-hydroxyethoxy-2,2,6,6-tetramethylpiperidine;
bis(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate; and
bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

- 5 18. A composition according to claim 11 which additionally contains another stabilizer selected from the group consisting of hydroquinone and monomethyl ether of hydroquinone.
19. A process for preventing the premature polymerization of a monomer polymerizable by free radical initiation which comprises
10 adding to said monomer (a) an effective amount of a combination of compounds of component (b) according to claim 11.
20. A process according to claim 19 for preventing the fouling of processing equipment including reactors, pipes, stills, distillation columns, cracking towers and heat transfer surfaces during the processing of a
15 monomer polymerizable by free radical initiation which comprises adding to said monomer, before processing is begun, an effective amount of a combination of compounds of component (b) according to claim 11.
21. A process according to claim 19 which comprises
20 adding 50 to 10,000 ppm of a mixture of components (i) and (ii), according to claim 13, in a weight ratio of from 1:10 to 1000:1, to a continuous feed stream to deactivate the autocatalytic polymerization, in any part of the continuous process equipment, of any ethylenically unsaturated monomer present in the feed stream, and
25 further adding to said feed stream an additional 10 ppm to 500 ppm of said mixture as a makeup additive to maintain the desired concentration of said mixture in the fluid feed stream being processed.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91810561.0

DOCUMENTS CONSIDERED TO BE RELEVANT			Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
Category	Citation of document with indication, where appropriate, of relevant passages			
X	US - A - 4 912 247 (P.V. ROLING) * Claims *	1-5, 7, 11-15, 18	C 07 C 69/54 C 07 C 57/075 C 07 C 15/46 C 07 C 67/62 C 07 C 7/20	
D, A	US - A - 4 668 721 (R. SELTZER et al.) * Column 3, line 45 - column 13, line 53; claims *	11-13		
D, A	US - A - 4 691 015 (R.A. BEHRENS et al.) * Column 1, line 45 - column 10, line 29; claims *	11-13, 18		
A	EP - A1 - 0 334 500 (UNIROYAL) * Claims *	1-5, 11-15		
				TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
				C 07 C 7/00 C 07 C 15/00 C 07 C 51/00 C 07 C 57/00
The present search report has been drawn up for all claims				
Place of search VIENNA		Date of completion of the search 07-10-1991	Examiner HOFBAUER	
CATEGORY OF CITED DOCUMENTS			T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document				

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